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Gold-Catalyzed Rearrangement of Alkynyl Donor−Acceptor Cyclopropanes To Construct Highly Functionalized Alkylidenecyclopentenes

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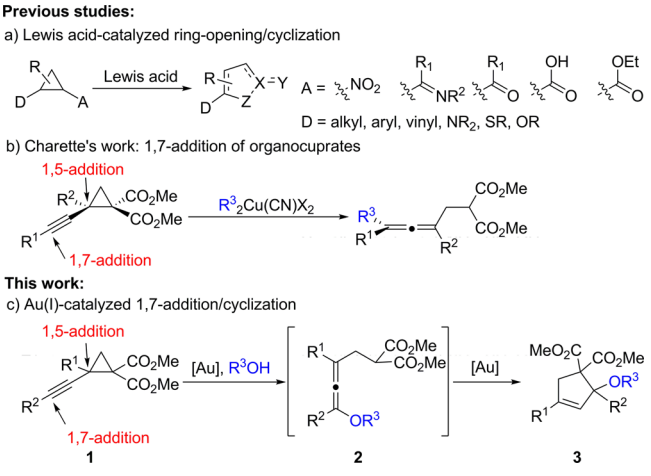
Supporting Information

ABSTRACT: A gold-catalyzed 1,7-addition−cyclization−elimination cascade sequence performed on a range of alkynyl-substituted donor−acceptor-type cyclopropanes provides facile entry to highly functionalized *exo*-alkylidenecyclopentenes under very mild conditions. Isolation of the relevant allyl ether intermediate helped shed light on the reaction's mechanistic course.

Donor−acceptor-substituted cyclopropanes[1] (DACs) are known to be competent substrates undergoing a variety of transformations, such as ring-opening,[2] cycloaddition,[3] and rearrangement reactions.[4] Their robust reactivities are largely attributed to high carbon−carbon bond polarization induced by the push−pull effect of the relevant vicinal donor and acceptor. Despite Wenkerst's and Reissig's pioneering works in the 1980s in this field, ring enlargements of DACs have gained attention only in recent years. In more recent studies,[4] Lewis or Brønsted acids are often used to coordinate to the acceptors and trigger the subsequent rearrangements. Charette[4f] and other groups[4a−e] reported the construction of pyrroles and dihydropyrroles using a ring-opening/cyclization of DACs, which can be considered as ring enlargement of DACs with imino substituents as the acceptors (Scheme 1a). Feng[5] reported an asymmetric version toward the chiral dihydropyrroles through a kinetic resolution process. Rearrangements of DACs would lead to dihydrofuran and furan derivatives when carbonyl groups (ketone,[4i] ester,[4h,j] and carboxyl[4g]) are used as acceptors, and this strategy has been successfully utilized in the total synthesis of several natural products.[4g,1c] Werz conducted a systematic investigation on reactivities of DACs by combining density functional theory (DFT) studies[6d] and experimental preparations of spiroketals,[6f] oligoacetals,[6e,g] bisthiophenes,[6a] oligopyrroles,[6b,c] and cyclic nitronates[4k] using a ring-enlargement strategy.

Scheme 1. Ring-Opening/Cyclizations of DACs



To the best of our knowledge, compared with the known studies on ring enlargements of DACs toward furan and pyrrole derivatives, there are few examples to construct all-carbon rings such as cyclopentane and cyclopentene derivatives which are important building blocks for many natural products and bioactive compounds.[7,8] Leveraged on the well-established gold activation mode of carbon−carbon triple bond,[9] we are motivated to uncovering a synthetic solution to such useful all-carbon structures through catalytic rearrangements of alkynyl DACs which have been successfully employed in [3 + 2]-cycloaddition[10] and 1,7-addition reactions (Scheme 1b).[11]

In the initial design summarized in Scheme 1c, the highly alkynophilic cationic Au(I) would induce the 1,7-addition on substrate **1** to give an allene intermediate **2**, which would undergo subsequent Au(I)-catalyzed cyclization to furnish cyclopentene structure **3**.

Conceivably, to realize the designed transformation, the activation of both the π-Lewis basic alkyne and the σ-Lewis basic esters might be needed to facilitate the initial C−C bond cleavage event. With cyclopropane **1a** as the model substrate, we employed the cationic Gagosz's catalyst PPh_3AuNTf_2 and $Mg(ClO_4)_2$ as the Lewis acids and MeOH as the nucleophile, anticipating the formation of 1,7-addition/cyclization product **3a**. The first trial gave alkylidenecyclopentene **4a** as the major product and enone **5a** as the minor one without detectable formation of **3a**, which was suspected to be unstable under the given reaction conditions and underwent further elimination to

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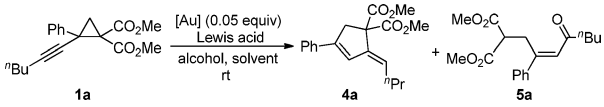
form **4a**. Solvent screenings (Table 1, entries 1−3) revealed that DCE gave a better selectivity and yield. When EtOH was used instead of MeOH, enone **5a** was obtained as the major product (entry 4). Control experiments revealed that σ-Lewis acid $Mg(ClO_4)_2$ is not necessary (entry 5). In the absence of MeOH, only the ring-opening product **6a** was isolated in 53% yield (entry 7). The absence of both alcohol and $Mg(ClO_4)_2$ can only lead to trace amounts of **4a** and **5a**. Then we investigated the effect of different alcohols (entries 8−12) and found that neopentanol gave a respectable 75% yield and that a relatively slow transformation was recorded when ^{t}BuOH was utilized (entry 11). From further screenings of counterions and Au catalysts (entries 12−17), the utilization of $PPh_3AuCl/AgSbF_6$ stood out to be optimal (85%, entry 15). In most trials, an impurity was observed, which was confirmed to be isomerized **7a** by NMR analysis.

With the optimal conditions identified, we next probed the scope of this new reaction (Scheme 2). A range of phenyls bearing various electron-donating and electron-withdrawing groups were examined, and all were found to give products in moderate to good yields and *E*/*Z* ratios (double-bond *E*/*Z* ratios of **4b−o** ranging from 7/1 to greater than 20/1). β-Naphthyl (**4p**, structure of (*E*)-**4p** was identified by X-ray crystallography[12]) and furyl (**4q**) also acted as suitable residues to furnish the desired products in acceptable yields. Alkyl-subsitituted DAC also delivered the desired product in 49% yield with the enone byproduct being formed in 32% yield as a mixture of *E*/*Z* isomers (**4s**). Notably, in the cases of **4c** and **4t**, presumably due to the conjugation-enhanced cation stabilization effects, the reactions were found to be prone to formation of ring-opening byproducts, which could be minimized to less than 5% by simply lowering the reaction temperature. Unfortunately, for the thienyl-substituted substrate (**4r**), lowering the temperature did not improve the reaction efficiency according to the ^{1}H NMR analysis of the crude reaction mixture (see the Supporting Information).

The effect of the alkyne residues was next examined, and their corresponding results were compiled in Table 2. Primary alkyls bearing phenyl and halogen delivered the desired product in acceptable yields (entries 1 and 2). Secondary isopropyl also led to the alkylidenecyclopentene as the major product, while cyclohexyl resulted a cyclopentadiene in 76% yield without any

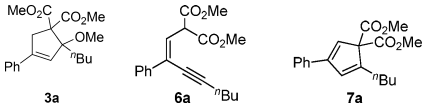
Table 1. Identification of the Optimal Reaction Conditions



1a 4a 5a

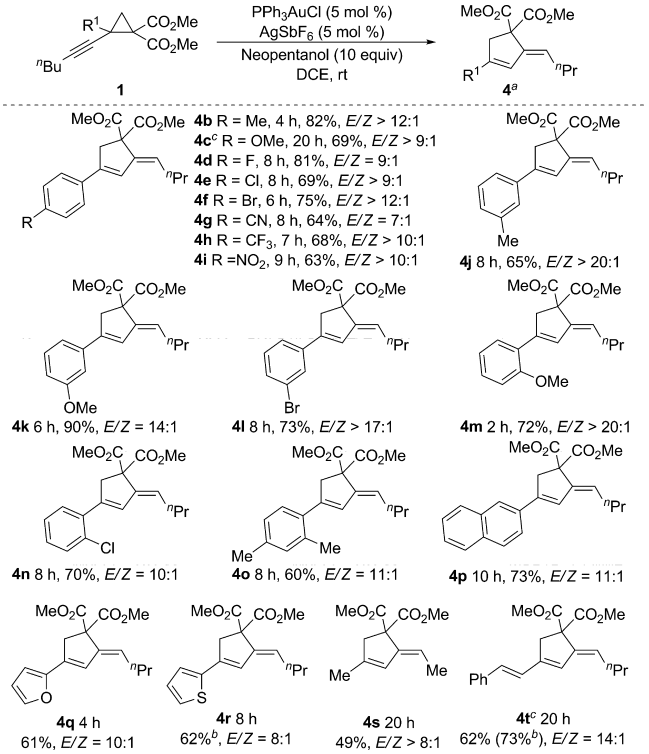
entry	[Au] (0.05 equiv)	solvent	alcohol (10 equiv)	**4a** yield (%) (*E*/*Z*)[a]	**5a** yield[a] (%)
1[b]	PPh_3AuNTf_2	DCE	MeOH	57 (84:16)	19
2[b]	PPh_3AuNTf_2	DCM	MeOH	43 (87:13)	32
3[b]	PPh_3AuNTf_2	PhMe	MeOH		
4[b]	PPh_3AuNTf_2	DCE	EtOH	21 (89:11)	57
5	PPh_3AuNTf_2	DCE	MeOH	60 (91:9)	16
6	PPh_3AuNTf_2	DCE		trace	trace
7[b,c]	PPh_3AuNTf_2	DCE			
8	PPh_3AuNTf_2	DCE	EtOH	58 (84:16)	16
9	PPh_3AuNTf_2	DCE	BnOH	66 (93:7)	
10	PPh_3AuNTf_2	DCE	cyclohexanol	44 (91:9)	trace
11	PPh_3AuNTf_2	DCE	^{t}BuOH	70 (88:12)	trace
12	PPh_3AuNTf_2	DCE	neopentanol	75 (93:7)	trace
13[d]	[Au]/AgOTf	DCE	neopentanol	66 (87:13)	trace
14[d]	**[Au]/$AgSbF_6$**	**DCE**	**neopentanol**	**85 (90:10)**	**trace**
15[e]	[Au]/$AgSbF_6$	DCE	neopentanol	75 (90:10)	15
16[f]	[Au]/$AgSbF_6$	DCE	neopentanol	26 (76:24)	30
17[g]	[Au]/$AgSbF_6$	DCE	neopentanol	35 (62:38)	22
18[h]	PPh_3AuNTf_2	DCE	BnOH		
19		DCE	EtOH		

[a]Determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene internal standard. [b]$Mg(ClO_4)_2$ (1.0 equiv) was added. [c]**6a** was obtained in 53% isolated yield. [d][Au] = PPh_3AuCl. [e][Au] = chloro[tris(*p*-trifluoromethylphenyl)phosphine]gold(I). [f][Au] = (John-Phos)AuCl. [g][Au] = IPrAuCl. [h]100 wt % of 4 Å MS was employed, no detectable reaction and substrate was recovered in 80% yield. DCE = 1,2-dichloroethane, DCM = dichloromethane, IPr = 1,3-bis(2,6-diisopropyl-phenyl)imidazol-2-ylidene, John-Phos = (2-biphenyl)di*tert*-butylphosphine.

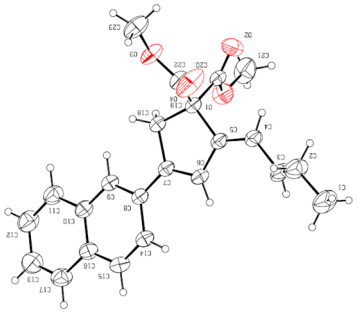


3a 6a 7a

Scheme 2. Reactivity Screenings on Substituent R[1]



[a]Isolated yields are used, and *E*/*Z* ratios were determined by NMR analysis of crude reaction mixtures. [b]Determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene internal standard. [c]Reaction was conducted at −10 to 0 °C with ice−salt bath.



X-ray crystal structure of (*E*)-**4p**

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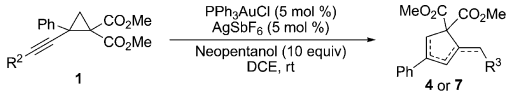
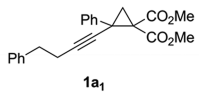
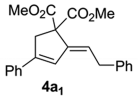
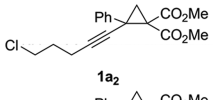
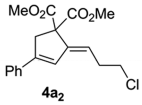
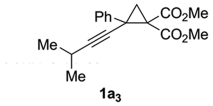
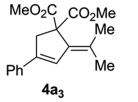
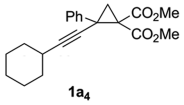
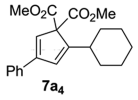
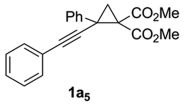
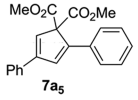
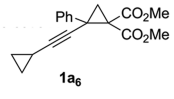
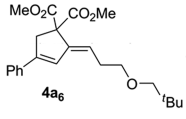
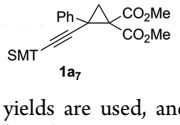
Table 2. Reactivity Screenings on Substituent R^2



entry	substrate	product	time (h)	yield (%)[a]	E/Z[a]
1	 **1a$_1$**	 **4a$_1$**	7	62	9:1
2	 **1a$_2$**	 **4a$_2$**	4	75	> 9:1
3	 **1a$_3$**	 **4a$_3$**	6	57	–
4	 **1a$_4$**	 **7a$_4$**	10	76	–
5	 **1a$_5$**	 **7a$_5$**	12	93	–
6	 **1a$_6$**	 **4a$_6$**	4	70	>19:1
7	 **1a$_7$**	decomposed	20	–	–

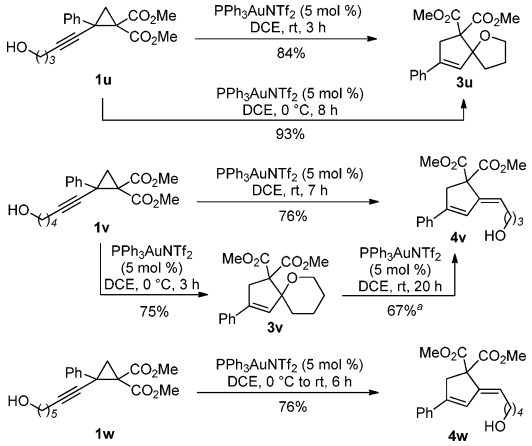
[a]Isolated yields are used, and E/Z ratios were determined by NMR analysis of crude reaction mixtures.

formation of the corresponding alkylidenecyclopentene, which apparently would be highly strained in this case (entry 3 and 4). With phenyl attached on the alkyne residue, the substrate was transformed into a multisubstituted cyclopentadiene in excellent yield (entry 5). Treatment of TMS-substituted alkyne (entry 7) only led to decomposition. The strained cyclopropyl was not tolerated and was formally opened by the addition of alcohol (entry 6, see the Supporting Information).

Substrates bearing internal hydroxyl groups were also synthesized and subjected to the standard conditions without addition of alcohols. As shown in Scheme 3, they displayed interesting reactivities responding to their tether size. Treating **1u** at room temperature provided a stable spiro bicyclic ether **3u** and only a trace amount of the subsequent elimination product. The product yield was further improved when the reaction was conducted at lower temperature (93% yield at 0 °C). For **1v**, running this reaction at room temperature led to alkylidenecyclopentene **4v** in good yield, and the appearance and subsequent consumption of spiro ether **3v** (which was independnetly prepared in 75% yield by lowering the reaction temperature to 0 °C) were clearly observed. For **1w** with extended tether, the expected alkylidenecyclopentene **4w** was exclusively delivered in 76% yield.

Krapcho decarboxylation of **4a** smoothly provided the corresponding monoester, while **7a$_5$** was transformed to cyclopentadiene under the same conditions (see the Supporting Information).

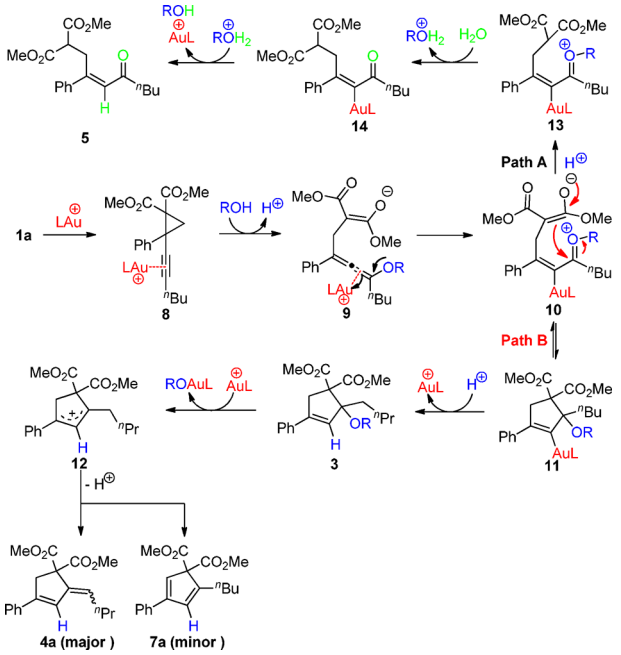
Scheme 3. Substrates Bearing Internal Hydroxyl Groups



[a]Determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene internal standard.

To account for the observed reactivities, a plausible reaction network is proposed and briefly depicted in Scheme 4.

Scheme 4. Plausible Reaction Pathway



Nucleophilic addition of alcohol[13] to the alkyne was likely triggered by alkynophilic Au(I) activation on **1**, thus giving rise to allene **9**[13] and vinylgold species **10**. In path A, starting from **10**, the enolate is captured by a proton and provides the observed byproduct **5** following hydrolysis and protodeauration. This process could be accelerated by a σ-Lewis acid $Mg(ClO_4)_2$ (Table 1, entry 4 vs entry 8). In path B, **10** undergoes cyclization and protodeauration to provide ether **3**, which is supported by the isolation of **3u** and **3v**. In most of cases examined herein, **3** was reactive enough and readily underwent elimination to give the products **4** and **7** through conceivably a π-allyl cationic intermediate **12**.[14]

In summary, we have designed and realized the Au-catalyzed 1,7-addition/cyclization/elimination cascade reaction on alkynyl donor–acceptor cyclopropanes under very mild conditions,

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thereby uncovering a synthetically robust entry to a range of highly functionalized alkylidenecyclopentenes. The direct isolation and characterization of spiro-bicyclic ethers laid experimental support on the proposed reaction pathways. The achievements recorded here should find utilities in the preparations of useful natural and unnatural substances bearing those structural motifs.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures and spectral data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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